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PHOTOCHEMICAL MODELING OF THE ANTARCTIC STRATOSPHERE:  
OBSERVATIONAL CONSTRAINTS FROM THE AIRBORNE ANTARCTIC OZONE EXPERIMENT  
AND IMPLICATIONS FOR OZONE BEHAVIOR

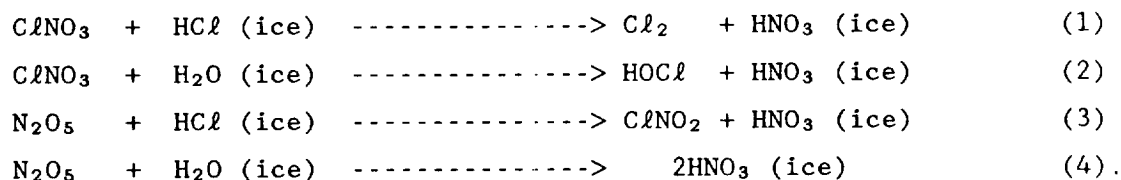
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The rapid decrease in O<sub>3</sub> column densities observed during antarctic spring has been attributed to several chemical mechanisms involving nitrogen, bromine, or chlorine species, to dynamical mechanisms, or to a combination of the above. Chlorine-related theories, in particular, predict greatly elevated concentrations of ClO and OClO and suppressed abundances of NO<sub>2</sub> below 22 km. The heterogeneous reactions and phase transitions proposed by these theories could also impact the concentrations of HCl, ClNO<sub>3</sub> and HNO<sub>3</sub> in this region. Observations of the above species have been carried out from the ground by the National Ozone Expedition (NOZE-I, 1986, and NOZE-II, 1987), and from aircrafts by the Airborne Antarctic Ozone Experiment (AAOE) during the austral spring of 1987. Observations of aerosol concentrations, size distribution and backscattering ratio from AAOE, and of aerosol extinction coefficients from the SAM-II satellite can also be used to deduce the altitude and temporal behavior of surfaces which catalyze heterogenous mechanisms. All these observations provide important constraints on the photochemical processes suggested for the spring antarctic stratosphere.

Results are presented for the concentrations and time development of key trace gases in the antarctic stratosphere, utilizing the AER photochemical model. This model includes complete gas-phase photochemistry, as well as the heterogeneous reactions:



Heterogeneous chemistry is parameterized in terms of surface concentrations of aerosols, collision frequencies between gas molecules and aerosol surfaces, concentrations of HCl/H<sub>2</sub>O in the frozen particles, and probability of reaction

per collision ( $\gamma$ ). Values of  $\gamma$  are taken from the latest laboratory measurements. The heterogeneous chemistry and phase transitions are assumed to occur between 12 and 22 km. The behavior of trace species at higher altitudes is calculated by the AER 2-D model without heterogeneous chemistry. Calculations are performed for solar illumination conditions typical of 60°, 70°, and 80° S, from July 15 to October 31.

The final products of heterogeneous processing by reactions (1)-(4) are very sensitive to the adopted initial concentrations of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2 + \text{ClNO}_3 + 2\text{xN}_2\text{O}_5$ ), to the adopted rates of (1) - (4), and to the degree of illumination during the processing. We consider four cases representing different initial conditions for  $\text{NO}_x$ , and different rates for the heterogeneous processing. These cases illustrate different possibilities for the behavior of antarctic trace species, given the existing uncertainties and the constraints placed by available observations. We have concentrated on the following measurements from AAOE: 1) column densities of  $\text{HCl}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$  and  $\text{ClNO}_3$  by the infra-red spectrometers aboard the DC-8 aircraft; 2) local densities of  $\text{NOY}$  ( $\text{NO}_x + \text{HNO}_3$ ) measured aboard the ER-2 aircraft; 3) local densities of  $\text{ClO}$  measured aboard the ER-2; 4) local densities of ozone measured aboard the ER-2; 5) column densities of ozone from the TOMS instrument.

Comparison of calculations and observations indicate the following:

- The observed column densities of  $\text{HNO}_3$  are consistent with mixing ratios of about 2.5 ppbv below 18 km near 70°, and of 1.5 ppbv deeper into the vortex. These values are also consistent with the ER-2  $\text{NOY}$  measurement.
- Calculated column abundances of  $\text{NO}_2$  are about 50% larger than observations. Since calculations indicate that most of this  $\text{NO}_2$  is located above 22 km for the denitrified conditions of antarctic spring, resolution of this discrepancy requires more careful consideration of modeling and measurements in this region.
- The calculated column densities of  $\text{HCl}$  are generally consistent with the low values observed, particularly if heterogeneous processing occurs throughout the month of September.
- Processing by (1) - (4) can yield substantial amounts of chlorine nitrate during August if initial  $\text{NO}_x$  concentrations during winter were of order 2 ppbv at 18 km. Negligible amounts of  $\text{ClNO}_3$  would be produced if initial

$\text{NO}_x$  abundances were a factor of two smaller. The high column densities of  $\text{ClNO}_3$  observed during September could be an indication of  $\text{ClNO}_3$  formation through reaction with  $\text{NO}_2$  from photolysis of nitric acid during this month, or that large amounts of  $\text{ClNO}_3$  present in August are not converted to active chlorine.

- Processing by (1) - (4) yields mixing ratios of  $\text{ClO}$  between 0.4 and 1.1 ppbv at 18 km during the early half of September.
- The decrease in local ozone densities observed by the AAOE instruments can be explained by chlorine-mediated catalytic cycles above 15 km. The  $\text{Cl}_2\text{O}_2$  cycle contributes about 80% of the calculated reduction, if we adopt currently accepted values for the formation and photolysis rates of  $\text{Cl}_2\text{O}_2$ , and assume that the photolysis produces molecular oxygen. Since there are still uncertainties in the above, these conclusions are dependent on future resolution of these issues.
- The calculated behavior of  $\text{ClO}$  after the end of the AAOE mission depends crucially on the amount of  $\text{HNO}_3$ , its photolysis rate, and the assumed duration of heterogeneous chemistry
- The calculated reduction in column ozone between August and October ranges from 40 to 110 Dobson units in the four cases considered, depending on the assumed concentrations of  $\text{NO}_x$ ,  $\text{HNO}_3$ , and the temporal extent of heterogeneous chemistry. Observations of  $\text{ClO}$  during late September and October would further constrain the above estimates.
- Calculated reductions in column ozone at different levels of chlorine exhibit a non-linear behavior. The calculated reduction accelerates for chlorine levels comparable to the adopted initial  $\text{NO}_x$  abundances during winter. Since these abundances also control the amount of processed  $\text{HCl}$ , the deepening of the ozone hole slows down for higher levels of chlorine in the future. Details of this behavior, however, are sensitive to the adopted  $\text{HNO}_3$  concentrations and rates of heterogeneous reactions, particularly of (2).